

# POLYMER HANDBOOK

THIRD EDITION

Edited by

J. BRANDRUP and E. H. IMMERGUT

F+E GB-X, 832 (Zust. Polymer Forschung)

Hoechst Aktiengesellschaft FRANKFURT (M) - HÖCHST	
18. III. 1993 * 1419	
Doc:	108017
Exp:	179180

Z 37/5



A WILEY-INTERSCIENCE PUBLICATION

JOHN WILEY & SONS

New York • Chichester • Brisbane • Toronto • Singapore

EXHIBIT

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# Viscosity-Molecular Weight Relationships and Unperturbed Dimensions of Linear Chain Molecules

M. Kurata and Y. Tsunashima

Institute for Chemical Research,  
Kyoto University,  
Uji, Kyoto-Fu, Japan

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## A. INTRODUCTION

### 1. The Viscosity-Molecular Weight Relationship

The limiting viscosity number  $[\eta]$  of a solution which has long been called the intrinsic viscosity is defined as

$$[\eta] = \lim_{c \rightarrow 0} \frac{\eta - \eta_0}{\eta_0 c} \quad (1)$$

in terms of the solvent viscosity  $\eta_0$ , the solution viscosity  $\eta$ , and

the solute concentration  $c$ . The concentration  $c$  is expressed in grams of solute per milliliter of solution or, more frequently, in grams of solute per 100 milliliters of solution, the limiting viscosity number being given in the reciprocal of these units, i.e., in milliliters per gram or in deciliters per gram. Here, following the IUPAC 1952 recommendations (1), we adopt the former unit. The quantity  $[\eta]$  of a polymer solution is a measure of the capacity of a polymer molecule to enhance the viscosity, which depends on the size and the shape of the polymer molecule. Within a given series of polymer homologs,  $[\eta]$  increases with the molecular weight  $M$ ; hence it is a measure of  $M$ .

Table C gives the limiting viscosity number—molecular weight relationships for polymers in various solvents and at various temperatures. The table contains the constants of the equation

$$[\eta] = KM^a \quad (2)$$

which is known as the Mark-Houwink-Sakurada equation.

It is now well established that for linear, flexible polymers, under special condition of temperature or solvent, (usually known as the Flory 'theta' temperature or solvent (2)), the above equation becomes

$$[\eta]_0 = K_0 M^{0.50} \quad (3)$$

The sign  $\theta$  in front of the temperature data in the table indicates that the viscosity constants were obtained under the  $\theta$  condition. Since Eq. (3) is approximately valid over the whole molecular weight range,  $K_0$  and  $a = 0.50$  may be used, without modification outside of the molecular weight range in which they were determined. However, it must be noted that  $[\eta]$  is rather sensitive to temperature in the vicinity of  $\theta$ , especially when  $M$  is bigger than  $5 \times 10^5$ .

In ordinary good solvents, the constants  $K$  and  $a$  obtained are valid only within a rather limited range of  $M$  (3,4). It is, therefore, quite probable that the tabulated relationships are in error outside the indicated range of  $M$  (see eighth column in the table). As for the effect of temperature, however, both  $K$  and  $a$  mostly become insensitive to the temperature when  $a$  exceeds about 0.70, and they may be used in a ten-degree range on either side of temperature at which the constants were determined.

The method of determination of the molecular weight and the number of fractionated samples (Fr.) or whole polymer samples (W.P.) used to determine the  $[\eta]$ - $M$  relationship are also given in the ninth and the sixth or seventh columns, respectively. The abbreviations used are as follows:

(A) Methods Yielding the Number-Average Molecular

Weight,  $M_n$   
 CR, cryoscopy  
 EG, end-group titration  
 VOS, vapor pressure osmometry  
 EB, ebullioscopy  
 OS, osmotic pressure

(B) Methods Yielding the Weight-Average Molecular

Weight,  $M_w$   
 LS, light scattering  
 SE, sedimentation equilibrium  
 SA, approach to the sedimentation equilibrium (Archibald's method)

(C) Empirical or Semi-Empirical Methods

EM, electron microscopy  
 GPC, gel permeation chromatography  
 LV, limiting viscosity number—molecular weight relationship  
 PR, analysis of polymerization rate (yielding  $M_n$ )  
 DV, diffusion and viscosity  
 MV, melt viscosity—molecular weight relationship  
 SD, sedimentation and diffusion  
 SV, sedimentation and viscosity

Thus, for example, the constants tabulated are for the  $[\eta]$ - $M$  relationships expressed in terms of  $M_n$  or  $M_w$  if the method is specified as OS or LS, respectively, i.e.,

$$[\eta] = K_n M_n^a \quad (4)$$

or

$$[\eta] = K_w M_w^a \quad (5)$$

The values of  $K_n$  and  $K_w$ , especially the former, are greatly influenced by the molecular weight distribution (MWD) of the polymer samples, and caution must be taken in using these relationships.

To illustrate this effect, let us assume that:

(i) Eq. (2) is applicable to the molecule  $i$  with molecular weight  $M_i$  over the whole range of  $M$ ; i.e.,

$$[\eta]_i = K M_i^a \quad (6)$$

(ii) The weight fraction  $w_i$  of the molecules  $i$  in a given sample can be represented by a continuous exponential function,

$$w_i(M_i) = [y^{h+1}/\Gamma(h+1)] M_i^h \exp(-y M_i) \quad (7)$$

$$y = h/M_n = (h+1)/M_w \quad (8)$$

or by the log-normal function,

$$w_i(M_i) = A M_i \exp[-p^2(\ln M_i/M_0)^2] \quad (9)$$

where  $h$ ,  $A$ ,  $p$ , and  $M_0$  are constants, and  $\Gamma$  represents the gamma function.

Then, since  $[\eta] = \sum w_i [\eta]_i$ , we obtain

$$K_n = K \Gamma(a+h+1)/h \Gamma(h+1) \quad (10)$$

$$K_w = K \Gamma(a+h+1)/(h+1) \Gamma(h+1) \quad (11)$$

for the exponential MWD, and

$$K_n = K (M_w/M_n)^{0.5(a+1)} \quad (12)$$

$$K_w = K (M_w/M_n)^{0.5(a-1)} \quad (13)$$

for the log-normal MWD (5). The values of  $K_n/K$  and  $K_w/K$  calculated by these equations are shown in Table B. This table may be used for estimating an error due to MWD in determination of  $M$ .

As an example, let us assume that a given polymer sample has the exponential MWD with  $M_w/M_n = 2.0$ , while an available  $[\eta]$ - $M_n$  equation has been obtained for samples with a narrow

MWD, e.g.,  $M_w/M_n = 1.1$ . Further, let  $a = 0.70$ . Then, to find the correct value of  $M_n$  of the given sample from  $[\eta]$ , we must use the equation (4) with  $K_s = 1.54K$ , instead of the available equation with  $K_s = 1.06K$ . Use of the latter would lead to an overestimate  $M_n'$  which is related to the correct  $M_n$  by

$$[\eta] = 1.54K M_n^{0.70} = 1.06K M_n'^{0.70} \quad (14)$$

The error amounts to about 70%, i.e.,  $M_n' = 1.7M_n$ . Thus, application of the viscosity equation written in  $M_n$  is to be restricted to within a narrow class of samples, unless an appropriate correction is made. On the other hand, if an  $[\eta]-M_n$  equation is available for the same pair of working and reference samples as above, we have

$$[\eta] = 0.951K M_n^{0.70} = 0.991K M_n'^{0.70} \quad (15)$$

instead of Eq. (14). Hence, the error  $M_n'$  amounts to only 6% ( $M_n' = 0.94M_n$ ), which will be negligible for more practical purposes.

Based on the above consideration, we classify the heterogeneity of polymers in four classes, A to D, as shown in the last column of Table B, and indicate it in the tenth column of Table C as a measure of the heterogeneity of the reference samples used.

It is desirable that readers select their own relationship by inspecting these data on heterogeneity as well as those on the number of samples and molecular weight range. Generally speaking, a 'good'  $[\eta]-M$  relationship is one that has been obtained on the basis of  $M_n$  for at least four samples of classes A and B (exceptionally C) or on the basis of  $M_w$  for those of class A (exceptionally B), whose molecular weights range over at least one half orders of magnitude.

In the 'Remarks' column of Table C, we have occasionally indicated by the letter R a 'recommended' relationship for the convenience of readers. In the range of low molecular weight (mostly less than  $10^5$ ), the constant  $a$  becomes 0.50 irrespective of solvent. This type of relationship can not be used, even approximately, at higher molecular weights. This case is noted by the letter L. High conversion polymers are also marked by the letter H, where the  $[\eta]-M$  relationships are less reproducible due to chain branching than are ordinary ones. The abbreviations used are as follows.

- A narrow MWD polymers, or well-fractionated polymers,  $M_w/M_n \leq 1.25$
- B ordinary fractionated polymers,  $1.30 \leq M_w/M_n \leq 1.75$
- C poorly fractionated polymers or most probable MWD polymers,  $1.8 \leq M_w/M_n \leq 2.4$
- D wide MWD polymers,  $M_w/M_n \geq 2.5$
- H high conversion polymers, including branches
- L limited to low-molecular-weight polymers
- R recommended relationship

In this table, polymers are arranged according to their structure in subgroups. Within each subgroup, the polymers are, in principle, given in alphabetical order. Within each polymer, the solvents are also arranged in alphabetical order, followed by the mixed solvents.

Chain configurational data are occasionally given in the first column. The data given in parentheses refer to only one set of viscosity constants listed in the same row, while the data given

without parentheses refer to a series of sets listed in the same and succeeding rows. Thus, for example, the data 'N content, 13.9 wt%' are effective only for the sixth row of cellulose trinitrate, and the data '95% *cis*, 1% *trans*, 4% 1,2' are effective for the fourth to eighth rows of polybutadiene.

Table C is essentially based on the table published by Kurata and Stockmayer (3). Data are also taken from tables published by Peterlin (7), Meyerhoff (8), Elias (9), and Krause (10), the last one including a number of unpublished data on acrylic and methacrylic polymers. We are also grateful to these authors. Thanks are tendered also to J. Brandrup and K. Kamide for their help with this compilation.

## 2. Unperturbed Dimensions of Linear Chain Molecules

The mean-square end-to-end distance  $\langle r^2 \rangle$  of a linear chain molecule in solution is usually expressed in terms of two basic quantities, the unperturbed mean-square end-to-end distance  $\langle r^2 \rangle_0$  and the expansion factor  $\alpha$ ; i.e.,

$$\langle r^2 \rangle = \langle r^2 \rangle_0 \alpha^2 \quad (16)$$

The latter quantity  $\alpha$  represents the effect of 'long-range interactions' which can be described as an osmotic swelling of the chain by the solvent-polymer interactions, while the unperturbed dimension  $\langle r^2 \rangle_0$  represents the effect of 'short-range interactions' such as bond angle restrictions and steric hindrances to internal rotation. The steric hindrances are also influenced by the torques exerted on the chain by solvent molecules, but the effect is rather small in many cases (11).

For sufficiently long chain,  $\langle r^2 \rangle_0$  becomes proportional to  $\Sigma n_i l_i^2$ , where  $n_i$  is the number of the  $i$ th-kind bond of length  $l_i$ . The quantity  $C_\infty$  defined by

$$C_\infty = \lim_{n \rightarrow \infty} \langle r^2 \rangle_0 / \Sigma n_i l_i^2 \quad (17)$$

is often called the characteristic ratio and it serves as a measure of the effect of short-range interactions.

The freely rotating state is a hypothetical state of the chain in which the bond angle restrictions are retained, but the steric hindrances to internal rotation are released. The mean-square end-to-end distance of the freely rotating chain  $\langle r^2 \rangle_{fr}$  can be readily calculated from the given basic structure of the chain. For instance, if the chain consists of only one kind of bond of length  $l$ , we obtain

$$\langle r^2 \rangle_{fr} = nl^2 \{ (1 - \cos \theta) / (1 - \cos \theta) \} \quad (18)$$

where  $n$  is the number of bonds and  $\theta$  is the supplement of the valence bond angle. For vinyl polymer chains,  $\theta = 1.54$  [rad],  $\cos \theta = 1/3$ , and  $n = M/m = 2M/M_0$ , and hence

$$(\langle r^2 \rangle_{fr} / M)^{1/2} = 0.308 / M_0^{1/2} = 0.218 / n^{1/2} \text{ [nm]} \quad (19)$$

where  $M_0$  is the molecular weight of the repeating unit and  $n$  is the average molecular weight per skeletal link. Similar expressions for  $r_{fr} (= \langle r^2 \rangle_{fr}^{1/2})$  can be obtained also for more complicated chains. The results are summarized in Table D.

The ratio of  $\langle r^2 \rangle_0$  to  $\langle r^2 \rangle_{fr}$ , then, represents the effect of steric hindrance on the average chain dimension:

$$\sigma = r_{fr} / r_{fr} = (\langle r^2 \rangle_0 / \langle r^2 \rangle_{fr})^{1/2} \quad (20)$$

The quantity  $\sigma$  is independent of  $n$ . Table E gives a list of the unperturbed dimensions of linear chain molecules which were